Unique Coating of Ruby Crystals on an Aluminum Oxide Wall by Flux Evaporation

Katsuya Teshima,* Atsushi Takano,† Takaomi Suzuki, and Shuji Oishi
Department of Environmental Science and Technology, Faculty of Engineering, Shinshu University, 4-17-1 Wakasato, Nagano 380-8553
†*Corporate Research and Development Division, Dai Nippon Printing Co., Ltd., 1-1-1 Ichigaya-Kagacho, Shinjuku-ku, Tokyo 162-8001*

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Ruby (Al_2O_3:Cr) layer was successfully grown on a wall surface of an aluminum oxide crucible by isothermal evaporation of molybdenum trioxide (MoO_3) flux. The growth was conducted by heating a mixture of MoO_3 and an oxide dopant (Cr_2O_3) at 1100 °C, for 5 h at this temperature without adding any reagent grade aluminum oxide. The ruby layers, obtained with a thickness up to 100–300 µm, were transparent-red. The layers consisted of ruby crystals having flat surfaces. This technique was found to be a very suitable method for coating ruby layer on aluminum oxide materials.

Ruby (Al_2O_3:Cr) is one of the most expensive gemstones and is the second hardest natural material known to mankind. Large rubies are rarer than equivalent diamond. Because of its excellent properties, including optical property, chemical stability, and mechanical strength, ruby is widely used in industry. Furthermore, corundum (including ruby and sapphire) layers have also attracted particular attention as insulators for electronic devices and as substrates for new energy devices.

Various techniques such as Verneuil, Czochralski, hydrothermal, vapor phase, and flux are commonly employed to synthesize ruby crystals.[1–11] However, few studies report on direct growth of ruby crystals on a substrate besides thin film growth of corundum. Many researchers have reported on the ruby growth in a platinum crucible by the slow cooling method using a system of lead compound fluxes, however, the grown crystals were of platelike habit.[6–9] Recently, we developed a unique technique,[10,11] which consists of isothermal evaporation of molybdenum trioxide (MoO_3), during the growth of ruby crystals having three-dimensional shape such as natural gemstones. The most important point of our technique is that MoO_3 flux perfectly disappeared from crucibles and only the objective crystals were left in crucibles. In this communication, we report on a unique technique of ruby layer coating on an aluminum oxide crucible wall.

Ruby layer was grown using a reagent grade MoO_3 as a flux. Aluminum oxide, which is the main component of ruby, was supplied from the wall of an aluminum oxide crucible. To give crystals their red color, an oxide dopant (Cr_2O_3) was added at a concentration of 0.03 wt % of the MoO_3. The flux (28.48 g) and the dopant (0.008 g) powders were weighed out, mixed together, and put into the aluminum oxide crucible with 42 mm (top) and 20 mm (bottom) in diameter and 36 mm in height. Al_2O_3 of the crucible is approximately 99.6% in purity. The lid was loosely fitted and the crucible placed in an electric furnace with silicon carbide heating elements. The crucible was heated at about 45 °C/h to 1100 °C, held at this temperature for 5 h and then cooled at a rate of 100 °C/h to 300 °C. Then, the crucible was removed from the furnace and allowed to cool rapidly to room temperature. After a heat treatment of 5 h at 1100 °C the flux evaporation ratio attained almost 100 wt %. To prevent the crucible from breaking by rapid cooling, the cooling at 100 °C/h was carried out. The transparent grown ruby layers were investigated and characterized by means of various techniques such as X-ray diffraction (XRD, Rigaku, RINT-1500) and electron probe microanalysis (EPMA, JEOL, JXA-8900R). The ruby layer was observed using an optical microscope (Keyence, VH-Z450+VH-7000C) and a scanning electron microscope (SEM, Hitachi, S-5000).

Figure 1 shows the aluminum oxide crucible which has the inner wall covered with a transparent-red layer (digital camera). The surface-treated aluminum crucible was observed under a halogen lamp. The cross-sectional image of the crucible wall covered with the transparent-red layer is shown in Figure 2 (optical microscope). The raw crucible wall was white and smooth

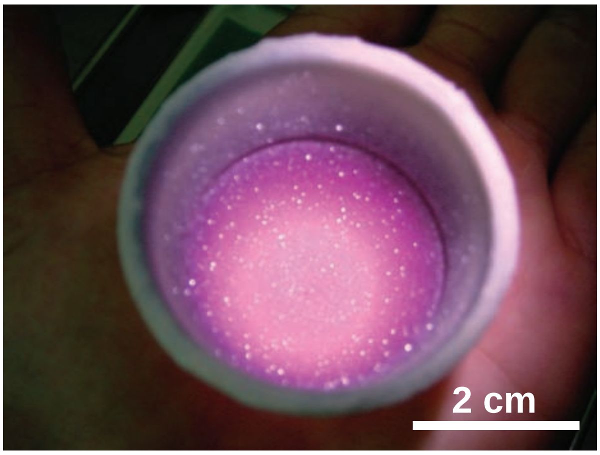

Figure 1. Photograph showing the aluminum oxide crucible with ruby layer.

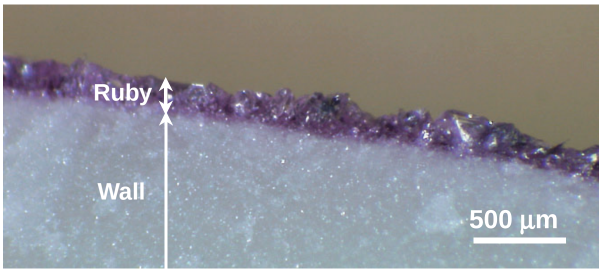

Figure 2. Optical micrograph showing cross-sectional image of the aluminum oxide crucible wall covered with the ruby layer.

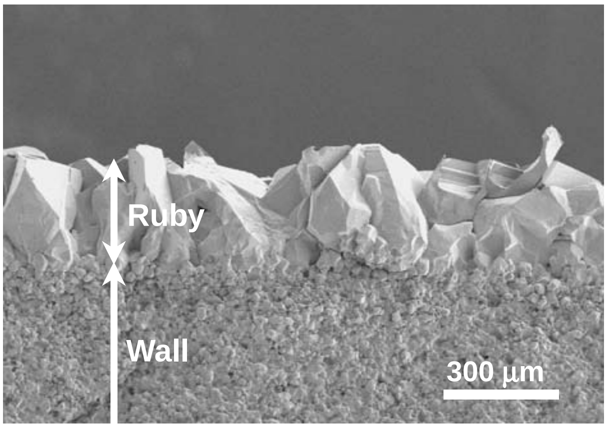

Figure 3. Scanning electron micrograph showing cross-sectional image of the aluminum oxide wall covered with the ruby layer.

surface. After the synthesis of ruby, the crucible inner wall changed from white into red, and sparkled with transparent-red crystals. The grown crystals were identified as ruby by their XRD patterns and EPMA profiles. The presence of chromium atoms, which gave the characteristic color, was confirmed in the transparent-red layer. On the contrary, no chromium atoms were detected in the white wall portion. The ruby crystallite layer with a thickness of about 100–300 µm was clearly observed on the aluminum oxide wall.

The interface between the ruby layer and the wall was readily observable in Figure 3 (SEM image). As clearly shown in this figure, the ruby layer is an aggregate of many single crystals (crystal sizes = 30–300 µm). The grown ruby crystals are much larger than alumina crystallites of the crucible wall. In addition, these crystals were surrounded by well-developed faces such as triangle and sexangle faces. The ruby layer were readily inseparable from the aluminum crucible wall.

Our synthesis technique has some industrial and ecological merits because the ruby synthesis temperature (max. 1100 °C) is approximately half of other melting growth techniques such as Verneuil and Czochralski methods and because the reagents used in this study are less harmful to human being and the environment. In addition, although the required equipments are very simple, the ruby layer, which consisted of many crystals having good crystallinity and well-developed faces, can be synthesized. Since the ruby layer directly grew on the aluminum oxide surface, they cannot be easily removed from the surface.

As mentioned above, our technique could become one of the most convenient and effective ruby (and other corundum) coating method. Furthermore, our coating technique might be applicable to other simple or complex forms of aluminum oxide materials such as wire, tube, substrate, ball, and various three-dimensional structures. Finally, since our growth model of ruby crystals resembles those of natural gemstones in druses, we may say that it is nature-mimetic crystal growth.

References

1 T. M. Maiman, *Nature*, **187**, 493 (1960).
2 E. A. D. White, *Nature*, **191**, 601 (1961).
3 D. Elwell, in "Man-Made Gemstones," Ellis Horwood Ltd., Chichester (1979).
4 D. Elwell and H. J. Scheel, in "Crystal Growth from High-Temperature Solutions," Academic Press, London (1975).
5 K. Watanabe and Y. Sumiyoshi, *J. Cryst. Growth*, **32**, 316 (1976).
6 R. C. Linares, *J. Appl. Phys.*, **33**, 1747 (1962).
7 D. F. Nelson and J. P. Remeika, *J. Appl. Phys.*, **35**, 522 (1964).
8 D. L. Stephens and W. J. Alford, *J. Am. Chem. Soc.*, **47**, 81 (1964).
9 S. Oishi, H. Kondo, T. Kobayashi, S. Watanabe, S. Wakabayashi, and Y. Sumiyoshi, *Nippon Kagaku Kaishi*, **1997**, 107.
10 S. Oishi, K. Teshima, and H. Kondo, *J. Am. Chem. Soc.*, **126**, 4768 (2004).
11 K. Teshima, H. Kondo, and S. Oishi, *Bull. Chem. Soc. Jpn.*, **78**, 1259 (2005).

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